Preparation and characterisation of two [70]fullerene diols, $C_{70}Ph_8(OH)_2$

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Reaction of a CCl_4 solution of $C_{70}Ph_8$ with air in the presence of light and [70]fullerene gives a bis-lactone $C_{70}Ph_8O_4$ (44%), together with a 1,2-diol, $C_{70}Ph_8(OH)_2$, 19,26,33,37,45,49,53,63-octaphenyl-7,8,19,26,33,37,45,49,53,63-decahydro[70]fullerene-7,8-diol (40%), **1** of C_s symmetry. This latter is also produced from reaction of a dichloromethane solution of $C_{70}Ph_8$ with 18-crown-6 and $KMnO_4$, together with another C_s symmetry diol, **2**, two possible structures for which are proposed; both **1** and **2** are the first diols to be derived from [70]fullerene. Whereas **1** is very insoluble in most organic solvents (but dissolves in THF), **2** is readily soluble in many organic solvents such as toluene, benzene, chloroform, carbon disulfide, and THF. The derivatives show appreciable differences in both their NMR spectra and their EI mass spectrometry fragmentation patterns.

Our researches on aryl derivatives of fullerenes produced by electrophilic aromatic substitution have resulted in the isolation of many products; thus far we have characterised $C_{60}Ar_5X$ (Ar = C_6H_5, 4-$MeOC_6H_4$, 4-FC_6H_4; X = Cl, H),[1,2] $C_{60}Ph_n$ (n = 2, 4),[3] $C_{70}Ph_n$ (n = 8, 10),[4] $C_{70}Ph_8O_4$,[5] $C_{70}Ph_9OH$,[6] a phenylated benzo[*b*]furano[60]fullerene,[7] a Diels–Alder adduct of $C_{70}Ph_8$ with anthracene (an example of cycloaddition at a 6:5-ring junction),[8] a phenylated isoquinolino[60]fullerene[9] and obtained evidence for numerous other components,[10,11] including (relevant to this work) the dihydro compound $C_{60}Ph_nH_2$ (n = 4, 10).[11] If substituted aryl rings are involved, then the number of potential fullerene derivatives is vast. Ascertaining the regiochemistry of these products and their mechanistic origins is a major part of our fullerene research.

On standing, $C_{70}Ph_8$ (produced by electrophilic substitution of $C_{70}Cl_{10}$ into benzene, with concurrent Cl_2 loss) undergoes spontaneous oxidative cage-opening to give a bis-lactone in a reaction which may involve the intermediate formation of a bis-vinyl ether.[5] During the preparation of $C_{70}Ph_{10}$ and $C_{70}Ph_8$ from $C_{70}Cl_{10}$, we isolated $C_{70}Ph_9OH$, the first fullerene to be described bearing a single hydroxy group attached to the cage.[6] Spontaneous oxidation of $C_{60}Ph_5H$ produces a benzo-[*b*]furano[60]fullerene,[7] and now we report that spontaneous oxidation of $C_{70}Ph_8$ produces in addition to the bis-lactone described above, a 1,2-diol, $C_{70}Ph_8(OH)_2$.

Hirsch and co-workers have also reported the formation of a 1,2-diol from a cyclopropanated [60]fullerene derivative.[12] We can also make diol **1** by their method, together with a second diol **2**.

Experimental

A mixture of [70]fullerene (0.8 mg) and $C_{70}Ph_8$ (64 mg) in CCl_4 (25 cm^3, neither dried nor distilled) was left to stand in the light. [70]Fullerene accelerates the reaction due, we believe, to the production of singlet oxygen, since it is known to be highly efficient in this latter respect.[13] ([60]Fullerene is even more efficient in producing singlet oxygen,[13] but was not added to the reaction mixture in case it complicated the difficult work-up procedure.) After four days the solution was evaporated to dryness; the residual solid was redissolved in toluene and purified by column chromatography (silica gel, toluene elution). [70]Fullerene and a trace of $C_{70}Ph_8$ eluted at the solvent front, followed by $C_{70}Ph_8O_4$ ($R_f = 0.36$) (44% yield, based on $C_{70}Ph_8$). A considerable quantity of material remained on the base line and was then eluted with dichloromethane–methanol (94:4) to give first some unidentified material, and then a pale yellow solution. On standing the latter yielded a pale yellow precipitate of $C_{70}Ph_8(OH)_2$ (**1**, 40% yield, R_f 0.125), which was insoluble in dichloromethane, carbon tetrachloride, acetone, pentane, diethyl ether, and chloroform; such insolubility is typical of fullerenols. The product is slightly soluble in benzene and toluene, and soluble in tetrahydrofuran.

The diol **1** can also be made by the crown ether oxidation procedure described by Hirsch and co-workers.[12] 18-Crown-6 (3.95 mg, 1.24 equiv.) and a 9.3×10^{-3} mol solution of potassium permanganate (1.61 cm^3, 1.5×10^{-5} mol) were added to $C_{70}Ph_8$ (17.6 mg, 1.21×10^{-5} mol) dissolved in dichloromethane (20 cm^3) and the mixture was stirred vigorously. The colour changed to light yellow, and the mixture was then treated with acetic acid (2 cm^3) and stirred for 30 min. The organic layer was separated, washed with water (10 cm^3), and dried ($MgSO_4$). The yellow solid remaining after removal of the solvent was dissolved in carbon tetrachloride, applied to a silica-gel column, and eluted with this solvent to give first a small quantity of unreactive impurity present in the starting material. Elution first with dichloromethane gave a mixture of two products (set aside for separation), and then with dichloromethane–methanol (94:4) gave **1**. The former mixture was re-purified by further chromatography (dichloromethane elution) and gave diol **2** as the main component (17% overall, $R_f = 0.79$); another component was present in very low yield and was not characterised.

EI mass spectra (70 eV)

Diol 1. The spectrum for **1** (Fig. 1a) shows the parent ion at 1490 amu, *cf.* 1491 required. However, hydrogen is readily lost from the OH groups, as revealed by the strong signal at 1489 amu (loss of hydrogen from both groups). Although the O/OH groups are lost quite readily (giving $C_{70}Ph_8H$ at 1458 amu), phenyl group loss is also fairly facile since there is a significant
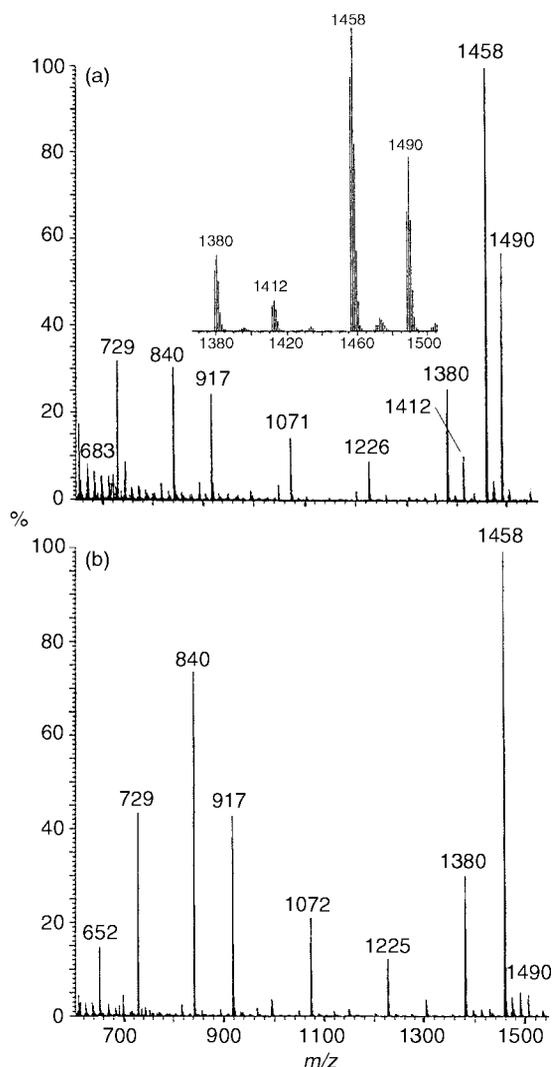
Fig. 1 EI mass spectra (70 eV) for (a) compound **1** and (b) compound **2**.

peak corresponding to $C_{70}Ph_7(OH)_2$ at 1412 amu. The stability of diol **1** is indicated by the intensities of the doubly-charged ion for both the parent and de-oxygenated species (at 745 and 729 amu, respectively).

Diol 2. The spectrum for **2** (Fig. 1b) is substantially different, the peak at 1490 amu being very weak indicating very facile loss of the OH groups, so that the 1458 amu peak is dominant here. This is the more customary behaviour for diols, which generally fragment under EI conditions. The instability of the parent ion here is also reflected in the lack of a doubly-charged ion at 745 amu, and the lack of a peak at 1412 amu which would correspond to the loss of a phenyl group from the diol; this contrasts with the spectrum for **1** where this peak is seen clearly.

IR spectra (KBr disc)

The IR spectra for **1** and **2** are shown in Figs. 2a and 2b, respectively, and both show the presence of OH groups. Though KBr spectra can be misleading because of moisture (and perhaps KOH) in the KBr, this is usually manifest only when the concentration of the analyte is small. In the present cases the transmission values cover a range of >40% in each case and in our experience, at these levels interference from the matrix is small. Overall the spectra are fairly similar, with common bands at 3058, 3030, 2924, 1598, 1493, 1446, 1384, 1260, 1187, 1033, 859, 756, 740, 725, 694, 664, 597, 591 and 453 cm^{-1}, due to the overall similar addended cage structure, and the dominance of aromatic signals.
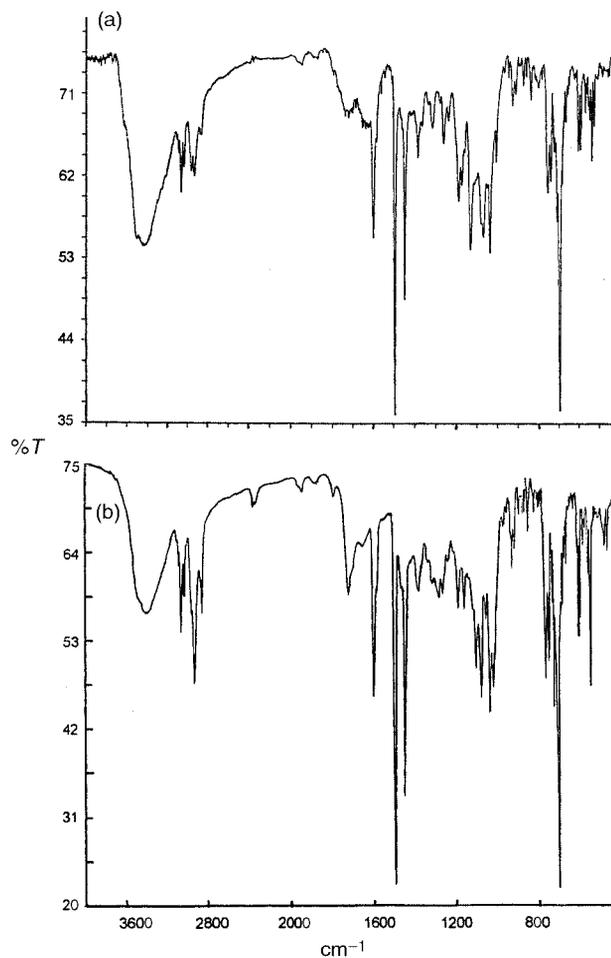

Fig. 2 IR spectra (KBr) for (a) compound **1** and (b) compound **2**.

^{1}H NMR spectra

Diol 1. The spectrum (d_8-THF solvent, 313 K, Fig. 3a) shows **1** to be C_s symmetric. The singlet at δ 7.36 (2 H intensity relative to those of the phenyl hydrogens) is confirmed as arising from OH since it is shifted to δ 7.47 at 298 K; all other peaks remain unchanged. This OH signal is much further downfield than that at δ 3.16 for $C_{70}Ph_9OH$ which may be attributed to mutual electron withdrawal by the adjacent OH groups or by hydrogen bonding; it is also more downfield than that at δ 5.13 for the diol derived from a C_{60} derivative.[11] However, no conclusions may be derived from the latter difference, because the addends involved are dissimilar. Although the locations of OH peaks are in general both temperature and concentration dependent, the differences observed above are larger than seem likely from these effects alone.

NOE analysis showed that the four sets of *ortho* hydrogens at δ 7.97, 7.63, 7.52, and 7.46 are due to phenyl rings D, C, A, and B, respectively (Fig. 4); the *meta* and *para* hydrogens were identified by 2D-COSY (both Double Quantum Filtered, and Hartmann–Hahn). As with other phenylated fullerenes (see *e.g.* ref. 4), the more downfield the signal for the *ortho* hydrogens for a given ring, the more downfield are the corresponding signals for the *meta* hydrogens relative to those for the *para* hydrogens. Thus here the differences $\delta_m - \delta_p$ are *ca.* 0, 0.45, 0.8 and 0.9 for rings D, C, A and B, respectively. For $C_{70}Ph_9OH$, the signals for the phenyl groups adjacent to the hydroxy group (and which were thus unambiguously identified) were notably downfield relative to those for the other phenyl groups. Likewise in **1**, the resonances for the phenyl groups (D) adjacent to the electron-withdrawing hydroxy groups are the most downfield (by *ca.* 0.17 ppm compared to the corresponding peaks in $C_{70}Ph_8$).[3] However, the (downfield→upfield) sequences of positions in the
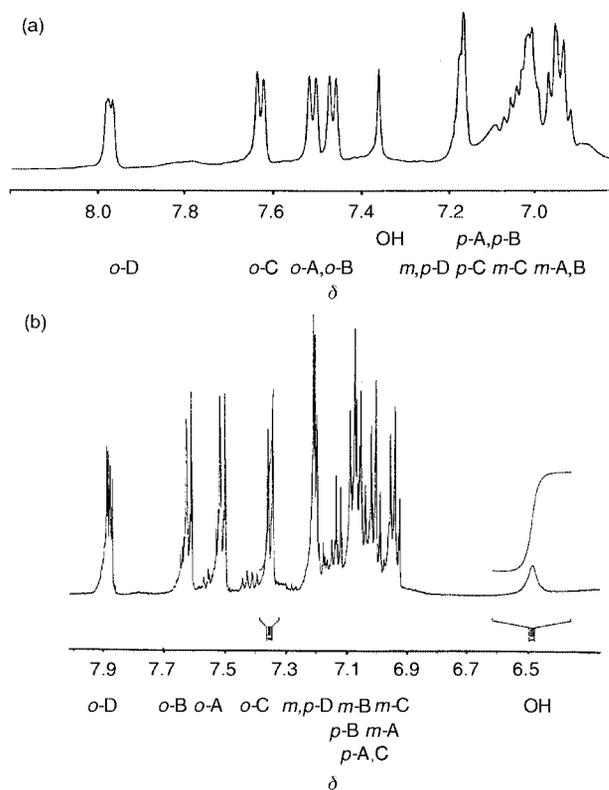
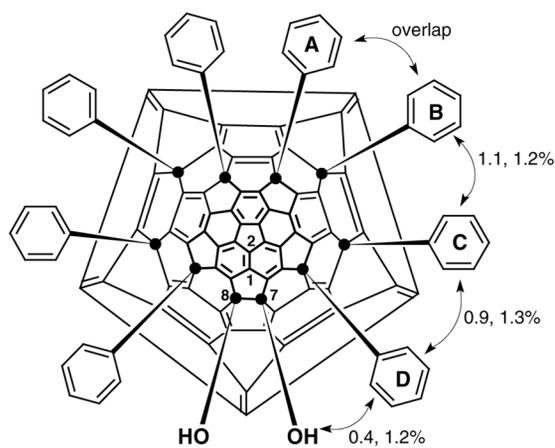Fig. 3 ^{1}H NMR spectra for (a) compound **1** and (b) compound **2**.

Fig. 4 Schlegel diagram for diol **1** showing the NOE couplings.

NMR spectrum for the *ortho* hydrogens of the corresponding phenyl groups A–D differ for the $C_{70}Ph_8$, $C_{70}Ph_{10}$, $C_{70}Ph_9OH$ and **1**, being DBCA, BACD, DABC, and DCAB, respectively. Clearly there is much yet to be learned concerning the operation of electronic effects in fullerenes.

Diol 2. The spectrum for **2** (CDCl$_3$, 313 K, Fig. 3b) shows it also to be C_s symmetric. A significant difference from the spectrum for **1** is that the singlet for the OH groups is broad and appears at δ 6.48; as for diol **1**, the integration shows a 2 H intensity relative to the hydrogens of the phenyl rings. NOE analysis (Fig. 5) shows four sets of *ortho* hydrogens which appear at δ 7.90, 7.62, 7.51, and 7.36 and are due to phenyl rings D, B, A, and C, respectively, so a yet further combination of the relative positions is obtained. For this isomer, the pattern of $\delta_m - \delta_p$ differences also increases in the downfield→upfield direction, being 0, 0.63, 0.66 and 1.14 for rings D, B, A and C, respectively. The identity of the OH hydrogen was confirmed by saturation transfer to water.
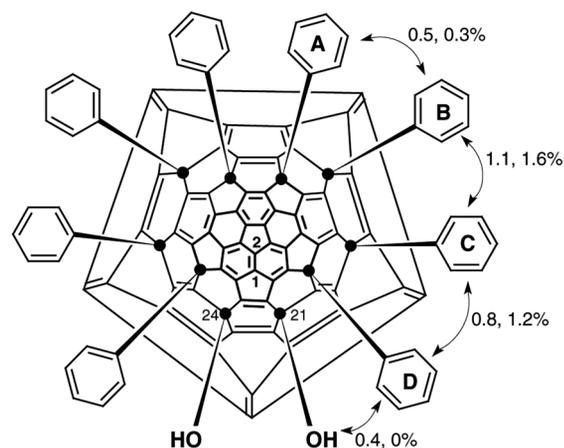

Fig. 5 Schlegel diagram for diol **2** showing the NOE couplings.

Comparison between the two isomers of the resonance positions for the *ortho* hydrogens of equivalent rings shows that the resonances for ring A are in almost the same position in both isomers, consistent with ring A being most remote from the OH groups. Likewise the resonance for ring D is marginally more downfield in isomer **1** since this ring is nearer to the presumed location of the OH groups. Surprisingly, however, the resonances for ring C are more downfield in isomer **1**, whilst those for ring B are more upfield; there is no obvious explanation for this.

^{13}C NMR spectra

Diol 1. The ^{13}C NMR spectrum (d$_8$-THF) for **1** contains 32 resonances (28 × 2 C + 4 × 1 C) for the cage in the sp^2 region as required for a C_s symmetry structure. These appear at (2 C intensity except where indicated): 176.86 (1 C), 159.24, 159.20, 157.49, 157.10, 156.23, 156.00, 155.84, 154.54, 154.49, 153.17, 152.40, 152.31, 151.84, 151.26, 150.37 (4 C, coincident peaks), 149.09, 148.42, 148.05, 147.62, 146.62, 145.35 (1 C), 144.65 (1 C), 143.18, 139.71, 138.86, 138.09, 137.38, 136.43, 134.16, 129.10 (1 C); the *ipso*-signals appear at 140.13, 139.64, 139.57 and 139.12 ppm. In the sp^3 region the peaks are at 95.18, 65.96, 62.50, 62.31 and 61.39 ppm, the former being attributed to the carbon bearing the hydroxy group. In $C_{70}Ph_9OH$ the sp^3 carbons bearing the OH groups appeared at 84.1 ppm, those bearing the phenyl groups appeared between 66.3 and 60.8 ppm.[6] In general the resonances in the diol are shifted downfield relative to those in $C_{70}Ph_8$ and $C_{70}Ph_{10}$.

The signals for the sp^2 carbons on the symmetry plane at 176.86, 145.35, 144.65 and 129.10 ppm are widely separated and much more so than for either $C_{70}Ph_8$ or $C_{70}Ph_{10}$. It is reasonable to assume that the 1,2-bond (see Fig. 4) is the one that is highly polarised, the resonance at 176.86 ppm being due to C1 and that at 129.10 being due to C2. No comparable analysis was possible for $C_{70}Ph_9OH$[6] because the C_1 symmetry makes all of the sp^2 carbon resonances indistinguishable.

Our assignment of structure for isomer **1** is based upon: (i) its formation during the spontaneous oxidation that produced also the cage-opened bis-lactone, which involved oxidative cleavage of the 7,8-bond; (ii) NOE evidence that the OH groups are in close proximity to the phenyl groups D; (iii) the similarity of the structure to that (unambiguously determined) for $C_{70}Ph_9OH$,[6] differing only in replacement of one phenyl group by OH. We therefore assign isomer **1** as 19,26,33,37,45,49,53,63-octaphenyl-7,8,19,26,33,37,45,49,53,63-decahydro[70]fullerene-7,8-diol.

Diol 2. The ^{13}C NMR spectrum (CDCl$_3$) also consists of 32 resonances (28 × 2 C + 4 × 1 C) for the cage in the sp^2 region as required for a C_s symmetry structure. These appear at (2 C intensity except where indicated): 157.42 (1 C), 157.34, 155.89,
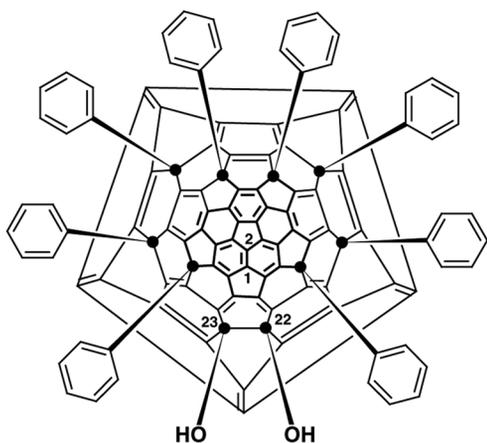
Fig. 6 An alternative structure for diol **2**. (NB: In order to keep the numbering consistent for the three diol structures, lowest locant numbering is not used here.)

155.57, 155.45, 154.76, 154.66, 154.57, 153.68 (1 C), 152.86, 152.37 (1 C), 152.36, 152.21, 151.86, 151.60, 151.16, 149.91, 149.81, 148.99, 148.69, 148.43, 148.20, 147.02, 146.97, 144.39, 143.38, 143.03, 138.65, 137.77, 135.80, 135.57 (1 C), 132.04; the *ipso*-carbon peaks are at 139.49, 139.24, 138.40 and 138.34 ppm. In the sp³ region the five required peaks are at 80.66, 62.00, 61.45, 60.91 and 60.73 ppm, and, as in the case of **1**, the resonances for the carbons attached to the phenyl groups are downfield relative to those in $C_{70}Ph_8$ and $C_{70}Ph_{10}$. The downfield carbon at 80.66 ppm is consistent with attachment to a hydroxy group.

Assignment of the structure for isomer 2

There are two feasible structures for diol **2**. In an attempt to identify the correct one, structural assignments for diols **1** and **2** and differences between the data are summarised as follows:

1. Diol **1** is much less soluble than diol **2**. This suggests that there is a significant difference in effective molecular size and hence hydrogen bonding between the two diols. It is possible to conjecture various scenarios involving either increased, or *decreased* intermolecular hydrogen bonding due to structural differences. Consequently this approach is not fruitful. We *can* conclude that there must be a significant structural difference between the two isomers, either in the relative locations of the hydroxy groups, or in the proximity of the phenyl groups to the hydroxy groups. We re-address these points below.

2. In general, diol **1** exhibits overall more downfield features in the NMR spectra compared to diol **2**, and this is particularly marked for the most downfield resonance in each spectrum. Thus for **1** and **2**, respectively, these are 7.97, 7.90 (*ortho*-H, ring D), 140.13, 139.49 (*ipso*-C), 95.18, 80.66 (sp³-*C*OH), 176.86, 157.42 (on-plane sp²-C). The locations of the OH groups for diol **1** (shown in Fig. 4) are the most consistent with these data. In particular, the OH groups are nearest to the phenyl groups D, nearest to one of the on-axis carbons, and adjacent to each other causing mutual downfield shift of the resonances for both the OH (probably aided by hydrogen bonding) and for the (sp³-*C*OH) groups.

3. Two possible structures are then available for diol **2**. One is as shown in Fig. 5, the other in Fig. 6. The structure in Fig. 5 involves 1,2-shifts of the OH groups (or more probably, the oxygens in the precursor). In this the OH groups are no longer adjacent, so that different physical properties could be expected. The OH groups lie midway between the on-plane sp² carbons, and so could be expected to cause the least downfield shift of their resonances. Also, the OH groups would not mutually withdraw electrons from each other, so that the sp³-COH carbons should appear more upfield as observed. The

OH groups are sufficiently near to the hydrogens of phenyl groups D to account for the observed NOE effect.

In the alternative shown in Fig. 6, the OH groups are in a 1,3-relationship compared to those in diol **1**. They could therefore arise from normal 1,3-rearrangements, or, since the OH groups are adjacent, from the usual alkene–KMnO₄→diol mechanism. Since the OH groups are adjacent as they are in **1**, the sp³ resonances for the carbons to which they are attached should probably appear well downfield as for isomer **1**, with similar solubility being observed (which is not the case). Moreover, they would also be in the same relationship to one of the on-plane sp² carbons as for isomer **1**, so the resonance for this carbon should presumably also appear much more downfield. (These arguments neglect the effect of the phenyl groups which are nearer to each of the carbons described above.) Since the distance between the OH groups and the *ortho*-hydrogens of phenyl ring D is significantly greater than in the above alternative, the observed NOE enhancement may be harder to rationalise; however, the OH group may be pointing towards phenyl group D so that an interaction may nevertheless be feasible.

Overall, there is no overwhelming evidence favouring either of the two possibilities, and no clear decision can be made between them.

We considered the possibility that in view of the markedly different mass spectrum for 'diol' **2**, and its greater solubility, it might be a dihydro compound. This can, however, be ruled out on four grounds. (i) Whilst we have detected many dihydro derivatives from arylation of fullerenes involving halogeno precursors, this is readily rationalised since halogenation is a radical process. Hence by the principle of microscopic reversibility, dehalogenation must also be a radical process, leading to fullerene radical intermediates which will abstract hydrogen from their surroundings in the customary radical manner. However, our oxidation does not involve any halogeno-fullerenes. (ii) The preparation involves oxidising conditions, hence formation of hydrides would not be expected. (iii) Both the ¹³C and ¹H NMR resonances for *C*-O*H* (80.66 and 6.48 ppm, respectively) are inconsistent with those for known hydrides. For example, in $C_{60}Ph_5H$ the corresponding values are 58.3 and 5.2 ppm, yet [60]fullerene is considerably more electron-withdrawing than [70]fullerene (as shown by the difference in chemical shifts for the di- and tetra-hydrides).[14] (iv) We have obtained the mass spectra for a wide range of dihydro-fullerenes and these show an *invariant* feature, *viz.* a parent ion at M amu and a major fragment at M − 2 amu. No such feature is apparent in Fig. 1a.

Oxidation

A surprising difference between diol **1** and that reported by Hirsch and coworkers is that we were unable to bring about further lead tetraacetate oxidation of **1** to the corresponding dioxetane or diketone. A possible reason may be that whereas the Hirsch dioxetane bridges across the junction of two six-membered rings, in our case it would have to bridge the junction between a six- and a five-membered ring. Such a bridge may cause too much strain in the latter ring.

Complexation

Difficulty was experienced in recovering, by chromatography, diol **1** from the solution containing $Cr(acac)_3$ used for the NMR spectroscopy; such chromatographic recovery is normally a straightforward procedure. This observation indicates that **1** complexes with this relaxation reagent.

Acknowledgements

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